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Supercritical CO2 for Semiconductor Applications
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Most readers are likely aware of the increasing popularity and number of emerging applications involving supercritical fluid carbon dioxide (CO_2). Recent reviews include the many polymerizations, syntheses, pharmaceutical applications, specialized materials fabrications, cleaning applications, food chemical extractions and chromatography that are conducted in supercritical fluids. While supercritical fluids have been adopted into common practices in some of these fields, they have only slowly gained interest from the semiconductor industry and are still considered novel in the context of a microelectronics fab. An overview of those recent accomplishments utilizing supercritical CO_2 that may be applied to semiconductor manufacturing was the topic of the presentation at recent SEMI Microelectronic Materials Strategy Symposium (M^2S^2) given by professor Christopher Ober (Cornell University, Department and Chair of Materials Science & Engineering).

Th Supercritical State

Supercritical fluids are compounds heated and pressurized above their critical pressure and temperature, at which point liquid and vapor states become indistinguishable and become a fourth, supercritical state. A characteristic unique to a supercritical fluid, being neither liquid nor vapor, is the liquid-like density that can be widely varied without introducing a phase interface. Simultaneously, a supercritical fluid has better transport properties than its liquid counterpart. The attractive capabilities of supercritical CO_2 arising from these properties (absence of surface tension from coexistence of liquid and vapor states, excellent mass-transfer phenomena, and controllable solvent quality) have been the impetus for recent innovative applications. Because the critical point of CO_2 is easy to achieve (31.1C, 1070.4 psi), CO_2 has become the solvent of choice for most supercritical applications. Organic cosolvents are often mixed with CO_2 to selectively improve solvation of polar functionalities, and the density and temperature of the fluid mixture are controlled to affect desired solvating potentials. Because CO_2 is cheap, non-toxic, non-flammable and recyclable, it presents an option for abatement of harsh chemicals and related expenses in microelectronics manufacturing.

Cl aning and Stripping

Photoresist and residue stripping, the pioneer microelectronics supercritical fluid platform, will likely be the first to be integrated into processing lines. Supercritical CO_2 cleaning, relying on selective is a cousin to the commercialized CO_2 snow cleaning systems that rely on physical mechanisms of particulate removal following CMP, etch, ion mill and metal lift-off steps. Supercritical cleaning and resist stripping will also occur inside clean rooms, contained in a single tool modular with patterning and developing tools. At least two collaborative commercial ventures (SC Fluids with Air Products & Chemicals, and Supercritical Systems Inc. with Praxair) are in development stages of equipment for supercritical stripping. (revised, 1/4/02)

Resist stripping systems generally incorporate a co-solvent with CO_2 (ie: 1% propylene carbonate is

used in Los Alamos' SCORR system) to bathe a wafer in a high-pressure chamber. Pressure pulsations and turbulence help dislodge particles of residue or debris, followed by a rinse with pure CO_2 to remove any cosolvent. The high viscosity and low surface tension of the fluid aid in penetrating materials and removing contaminants. Biberger, of Supercritical Systems, has shown results of resist removal post-oxide etch or post-metal etch without damaging the underlying metal structures while also boasting shorter strip times than used in conventional systems. Resist removal without damaging underlying low-□ SiLK dielectric is another strong selling point of the system, as many proposed low-□ materials lack mechanical or chemical strength and are damaged by traditional cleaning techniques.

Polar-head fluorinated and non-fluorinated surfactant molecules for reverse-microemulsion assisted contaminant removal have been synthesized as another tool for CO_2-cleaning systems. These cleaning strategies can also be applied to initial wafer surface cleaning, since solubility of non-polar organic compounds from greases, oils, and fingerprints is high in supercritical CO_2.

Resist Technologies

Beyond stripping, additional photoresist technologies: drying, selective developing and spinning have been conducted in CO_2. It is projected that the incorporation of an in-house CO_2 supply and recycling system for cleaning applications will lower the activation barrier for incorporation of these other CO_2 applications.

Pattern collapse of structures, a phenomenon related to the surface tension of rinse solution and a function of spacing and aspect ratio of patterns, becomes an increasingly serious problem, as smaller features are desired. Lateral forces caused by interfacial tension lead to deformities and failures of patterns. Excellent success using supercritical drying to prevent collapse has been demonstrated on MEMS and silicon structures. By performing an exchange step to replace resist rinse liquid with supercritical fluid, then gradually reducing pressure until vapor is present, the rinse liquid can be 'dried' without allowing the presence of a liquid/vapor interface. Ethanol rinse liquid can be directly replaced with supercritical CO_2, whereas water rinse liquid must be replaced by surfactant-containing CO_2 or by surfactant-containing hexane prior to CO_2 exchange. Resist patterns with aspect ratios of at least 7.5 (20 nm wide) have been produced using these drying techniques in a resist drying apparatus designed by NTT Laboratories.

Direct development of resists by CO_2 offers advantages of chemical abatement while reducing processing steps (drying and developing are one step) for a cheaper and environmentally green lithography. When pure CO_2 is desired as a developer, novel resists must be synthesized. Block copolymers with acid-cleavable tetrahydropyranl groups and CO_2 soluble, fluoro-side-chain-containing methacrylate groups have been patterned at 193 nm and E-beam as negative-tone chemically-amplified resists and developed in pure CO_2 at Cornell. Our current research on 157 nm resists, which often contain F to increase transparency, may lead to CO^2 soluble 157 nm resists as well.

Spin-coating from liquid CO_2, another application in research stages, also requires synthesis of CO_2-soluble polymers. DeSimone, (University of North Carolina, Chapel Hill), the holder of multiple patents on the technique, suggests that spinning may provide the capstone on a green lithography platform: spinning, developing, drying and stripping of a resist by using CO_2 in various states with various combinations of cosolvents.

Metal Deposition

Chemical fluid deposition (CFD) of metals is another supercritical application of rising interest. Metals including copper and nickel have been deposited onto silicon by the reduction of organometallic compounds with hydrogen within a supercritical CO_2 carrier. James Watkins, University of Massachusetts, developer of CFD cites advantages including conformal coverage on complex surfaces and unprecedented filling of high-aspect-ratio via features where current CVD and PVD techniques are not viable. Depositions can be conducted at low temperatures (40 - 80 C) using precursors with comparatively benign effluents. High purity of the resultant films is facilitated by high solubility of the

ligand by-products in CO_2.

Silylation of silicon wafers (McCarthy, University of Massachusetts) as well as etching of resist have also been conducted in supercritical CO_2 carrier media. In both applications, the use of supercritical fluid as a carrier for the silane reagents or the etchant gas reduces the consumption of chemicals and improves surface coverage rate by capitalizing on the low surface tension of the supercritical state.

Novel Applications

Inventive supercritical CO_2 applications suggesting novel modifications to the microelectronics-processing scheme are also being researched. Directly patternable dielectric materials have been demonstrated from CVD deposited F-containing precursors by Gleason (MIT) and Ober (Cornell). After E-beam patterning, the low-k film was developed in supercritical CO_2. Although research on patternable low-k materials is incomplete, production of such materials would eliminate cost and chemicals related to several pattern-transfer steps of IC manufacturing, and the promise is alluring.

Other applications include polymer foaming by supercritical fluid to form low-k interconnect materials (patent held by Micron Technologies), and removal of metals and inorganic contamination by reacting the inorganic contamination with a conversion agent before removing with a solvent in supercritical fluid CO_2 (patent held by TI).

Future

The scope of research touched upon here indicates that supercritical technology may one day become as common in the semiconductor industry as it has in the pharmaceuticals and food industries. It is both the environmental and technological advantages of supercritical CO_2 that make this technology extremely attractive to semiconductor manufacturers. The future of cleaning with non-toxic, non-flammable, recyclable, solvents will eliminate exposure to harmful chemicals without generating aqueous waste. CO_2 cleaning will be found soon in fabs, but a slow adoption rate by semiconductor manufacturers will keep prices of SCF systems high in the meantime.

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